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X-ray intensities and structural studies of the spinel $MgCr_2O_4$

V M Nanoti and D K Kulkarni
Department of Physics, Institute of Science, Nagpur-440 001, India

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Abstract : Assignment of space group for the compound $MgCr_2O_4$ aroused many controversies. Compound being cubic spinel, usual assigned space group is Fd3m. But critical study of $MgCr_2O_4$ showed some additional reflections, which are not permitted by space group Fd3m. Grimes suggested the space group $F\bar{4}3m$ for the same. A comparative study of X-ray intensities of the compound by using both the space groups Fd3m and $F\bar{4}3m$ is carried out in the present work.

Keywords : Cubic spinel, intensity calculations, space group assignment

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A group of oxides with formula XY_2O_4 with crystal structure of either $MgAl_2O_4$ or Mn_3O_4 is known as spinel. These spinel structures are cubic or tetragonal unit cells respectively, which have similar atomic arrangements in a unit cell. The space group associated with the cubic structure is Fd3m ($MgAl_2O_4$) in which B-sites have 3m point symmetry [1]. Many binary spinels containing Mg^{+2} are studied by various workers and explained the results on the basis of previously well-tested space group Fd3m. Later on, critical study of $MgCr_2O_4$ [2-5] is carried out indicating that there are some additional reflections which are not permitted by space group Fd3m. These extra reflections are linked [6-9] with displacement of B-cations (Cr^{+3}) along [1,1,1] direction which in effect reduces the point symmetry to 3m with space group $F\bar{4}3m$. The oxides of Mg^{+2} found to be controvarsial due to iso-electronic scattering with O^{-2} for X-rays.

It is interesting to know that all compounds with XY_2O_4 need not have spinel structure *e.g.* $BeAl_2O_4$, $MgSi_2O_4$ *etc.* So complete structure along with exact space group can only be known if atomic positions are determined by systematic matching of intensities. Intensity depends upon scattering powers of the atomic centre and vary with 'λ' and 'T'. Assuming

effect of 'T' to be very small, one can estimate intensities sufficiently accurate for the purpose of structure determination. We calculated intensities for the cubic spinel $MgCr_2O_4$ using both the space group Fd3m and $F\bar{4}3m$.

Intensity for non-zero reflections can be computed using the formula

$$I_{hkl} = \left| F_{hkl} \right|^2 . P. \frac{1 + \cos^2 2\theta}{\cos \theta . \sin^2 \theta},$$

where symbols have usual meanings.

The amplitude of structural factor $[F_{hkl}]$ is obtained from the expression

$$\left| F_{hkl} \right| = \left[\left(f_r A_r \right)^2 + \left(f_r B_r \right)^2 \right]^{1/2}.$$

The values of A and B factors for space groups $F\bar{4}3m$ and Fd3m are first calculated [10].

The intensities for all the observed planes are then calculated. Values of I/I_{max} (observed), I/I_{max} (for Fd3m) and I/I_{max} (for $F\bar{4}3m$) for all the planes are listed in the Table 1.

Table 1. A comparative study of the intensities

h k l	Observed I/I_{max}	I/I_{max} (cal) (Fd3m)	I/I_{max} (cal) ($F\bar{4}3m$)
220	14	11.97	11 93
311	100	100.00	100 00
222	14	10 56	10 60
400	55	52.99	52 95
422	4	3 26	3.66
511	40	25.27	38 82
440	55	38.82	38.82
531	14	10.48	10.50
620	40	13.08	13 08

Our results based on both the space groups show that the changes in the intensities are very small and one can not be sure enough to say that the compound possesses the space group $F\bar{4}3m$. There appears to be a large degree of difference between the report in the intensities of $MgCr_2O_4$. The most intense plane for 440 then 311 plane may not be due to displacement of Cr^{+3} ions as suggested earlier, but may be due to the ordering of cations and formation of superlattice and/or constructing interference of Mg^{+2} and O^{-2} ions which are isoelectronic and have similar scattering powers. So there is no necessity of changing the

space group from Fd3m to $F\bar{4}3m$. Some of the forbidden reflections may be explained on the basis of superlattice formation just like alloys.

Acknowledgments

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References

[1] A B Devale *PhD Thesis* (Nagpur University) (1980)

[2] N W Grime and R J Hilleard *J.Phys.* **C3** 866 (1970)

[3] N W Grimes and A J Collet *Phys. Stat Sol.(b)* **43** 591 (1971)

[4] N W Grimes *Phil. Mag.* **26** 1217 (1972)

[5] N W Grimes *J. Phys.* **C6** L78 (1973)

[6] R J Hilleard *J. Phys.* **C8** L193 (1975)

[7] C Infante and B E F Fender *J. Phys.* **C6** L333 (1973)

[8] E J Samuelsen *J. Phys.* **C7** 115 (1974)

[9] E J Samuelsen and O Steinsvoll *J. Phys.* **C8** L427 (1975)

[10] *International Tables for X-ray Crystallography* **Vol III** (Dordrecht D Reidel) (1952)